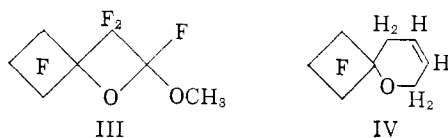
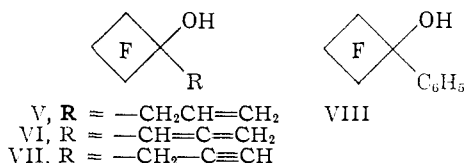


for 12 hours at 300° in a sealed tube. However, ketones with fluorine atoms attached to both α -carbon atoms have been shown to have unusual chemical properties,² and the added effect of ring strain in I enhances its reactivity. In many reactions the carbonyl group takes part in formation of four- and six-membered rings, and a large number of unusual additions to the carbonyl group have been observed.

Reaction of I with methyl trifluorovinyl ether at room temperature gave 2,3,3,5,5,6,6,7,7-nonafluoro-2-methoxy-1-oxaspiro[3.3]heptane (III, b.p. 98°, 91% yield; *anal.* Calcd. for $C_7H_3O_2F_9$: C, 29.0; H, 1.0; F, 59.0. Found: C, 29.2; H, 1.3; F, 58.7). Compound I behaves as a potent dienophile as illustrated by its reaction with butadiene below 0° to give quantitatively the adduct IV, b.p. 84° at 110 mm. (*anal.* Calcd. for $C_8H_6F_6O$: C, 41.1; H, 2.6; F, 49.1. Found: C, 41.5; H, 2.8; F, 49.0).

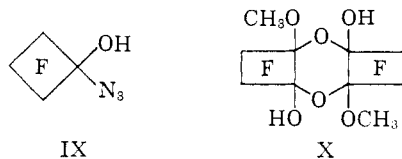


Perfluorocyclobutanone (I) reacts at room temperature with a variety of unsaturated compounds to give cyclobutanols. For example, propylene gave the allylcyclobutanol V, b.p. 114°, 88% yield; *anal.* Calcd. for $C_7H_6OF_6$: C, 38.2; H, 2.8; F, 51.8. Found: C, 38.4; H, 2.8; F, 51.4. Similarly methylacetylene gave the allene VI (b.p. 121°, 53% yield) and allene gave the acetylene VII (b.p. 116°, 47% yield). *Anal.* Calcd. for $C_7H_4OF_6$: C, 38.6; H, 1.9; F, 52.3. Found for VI: C, 39.1; H, 2.1; F, 51.8. Found for VII: C, 38.7; H, 2.1; F, 52.1.



Aromatic compounds add readily to I. For example, benzene reacts below 25° in the presence of aluminum chloride catalyst to give the phenylcyclobutanol VIII, b.p. 134° at 130 mm., 96% yield; *anal.* Calcd. for $C_{10}H_6F_6O$: C, 46.9; H, 2.4; F, 44.5. Found: C, 47.0; H, 2.8; F, 44.5.

The first isolable azidocarbonyl (IX) was obtained by the reaction of hydrazoic acid with I at -15° in methylene chloride. The product distilled at 34° at 20 mm., m.p. 4-5.5° (77% yield). *Anal.* Calcd. for $C_4HF_6N_3O$: F, 51.6. Found: F, 51.6. Small samples exploded when held in a flame.



(2) H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960).

Perfluorocyclobutane-1,2-dione (II), b.p. 35°, was synthesized in 30-50% yields by sulfuric acid hydrolysis of 1,2-dimethoxyperfluorocyclobutane, prepared in 83% yield by thermal dimerization of methyl trifluorovinyl ether at 150° (*Anal.* Calcd. for $C_4F_4O_2$: F, 48.7; mol. wt., 156. Found: F, 48.7; mol. wt., 157.5 by vapor density).

The blue color undoubtedly is related to the required *cis* relationship of the two carbonyl groups in the four-membered ring along with the strong inductive effect of the fluorine atoms. The linear perfluoro-1,2-diketone, $C_3F_7\text{COCOC}_3F_7$,⁴ is yellow. Leonard and Mader⁵ have shown that in alicyclic 1,2-diketones having no α -hydrogens the long wave length absorption varies regularly as the angle between the planes of the carbonyl groups is decreased by decreasing ring size. Shoppee⁶ has reported that 4,4,5,5-tetramethyl-1,2,3-cyclopentanetrione is blue. Perfluorocyclobutane-1,2-dione gives no e.p.r. signal, so the color cannot be ascribed to free radical character.

The blue diketone II polymerizes easily but can be kept unchanged over phosphorus pentoxide. Reaction with methanol gave mainly the bis-methylhemiketal,⁷ m.p. 39-42° (*anal.* Calcd. for $C_6H_8F_4O_4$: F, 34.7. Found: F, 34.7); however, a small amount of the dioxane X or isomer thereof, m.p. 182-183°, was also formed. (*Anal.* Calcd. for $C_{10}H_8F_8O_6$: C, 31.9; H, 2.1; F, 40.4; mol. wt., 376. Found: C, 32.1; H, 2.6; F, 39.9; mol. wt., 365 (ebullioscopic in acetone).)

The diketone II also underwent many of the unusual reactions of the monoketone I, for example with dienes, propylene, methyl trifluorovinyl ether and aromatic compounds. Reaction occurred at one and both of the carbonyl groups in addition to formation of some dioxane-hemiketal structures analogous to X.

Details on the preparation and reactions of these perfluorocyclobutanones will be reported in future publications.

(3) D. I. McCane, U. S. Patent 2,982,786 (1961).

(4) J. J. Drysdale and D. D. Coffman, *J. Am. Chem. Soc.*, **82**, 5111 (1960).

(5) N. J. Leonard and P. M. Mader, *ibid.*, **72**, 5388 (1950).

(6) C. W. Shoppee, *J. Chem. Soc.*, 269 (1936).

(7) Prepared by Dr. R. M. Scribner of these laboratories.

CONTRIBUTION No. 691

CENTRAL RESEARCH DEPARTMENT

EXPERIMENTAL STATION

DAVID C. ENGLAND

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WILMINGTON, DELAWARE

RECEIVED APRIL 3, 1961

A HIGHER HYDRIDE OF YTTERBIUM

Sir:

The rare-earth metals, with two exceptions, are known to react with hydrogen at moderate temperatures and atmospheric pressure to form hydrides approaching RH_3 .¹ The lighter rare-earth trihydrides have a face-centered cubic structure while those of samarium and beyond are hexagonal

(1) A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, **146**, 149 (1925); R. Viillard, *Compt. rend.*, **221**, 144 (1945); R. N. R. Mulford and C. E. Holley, Jr., *J. Chem. Phys.*, **59**, 1222 (1955); W. L. Korst, Ph.D. Thesis, University of Southern California, 1956; V. I. Mikheeva and M. E. Kost, *Doklady Akad. Nauk S.S.S.R.*, **115**, 100 (1957); R. Streck and K. Dialer, *Z. anorg. allgem. Chem.*, **306**, 141 (1960).

closest-packed. The two exceptions are europium and ytterbium, which form orthorhombic dihydrides.² We wish to report the synthesis of a noteworthy higher hydride of ytterbium.

For our investigations of rare-earth hydrogen systems in regions of high dissociation pressures (up to 65 atm.), we constructed a stainless steel high-pressure system. This consisted of an atomic hydrogen welded,³ double-walled bomb, in which the outer chamber could be pressured with hydrogen to prevent diffusion from the inner bomb at the high temperatures. Accessories consisted of a 0-1000 p.s.i. Bourdon gauge and a steel reservoir of uranium hydride for pressuring the system.

The ytterbium-hydrogen system was of particular interest since it seemed likely that the predicted thermodynamic stability of a trihydride phase placed it within range of attainable high pressures. The inner bomb was charged with eight grams of cleaned, 99.8% ytterbium metal⁴ and first heated *in vacuo*. It then was allowed to absorb hydrogen at atmospheric pressure until the composition of the hydride was YbH_{1.90}. The hydrogen pressure in the apparatus was increased to several atmospheres and pressure-temperature-composition data obtained. At a composition of YbH_{2.4} the dissociation pressure was 20.9 atm. at 312°. Upon completion of the experiments, the sample was removed from the bomb in a protective atmosphere. It was a black, air-stable substance; a 94 mg. sample stored in air for 70 days gained less than 1 mg. Examination by powder X-ray diffraction techniques showed the presence of a f.c.c. phase along with a small amount of the orthorhombic dihydride. The lattice constant of the f.c.c. phase was determined, after correction for film shrinkage, from a plot of *a* versus the Nelson-Riley function, and found to be 5.192 ± 0.002 Å. A calculation of the expected lattice constant for a f.c.c., BiF₃-type ytterbium trihydride using 0.86 Å. for the radius of the Yb⁺³ ion⁵ and correcting for the increased coordination number, and 1.29 Å. for the radius of the hydride ion⁶ gave *a* = 5.14 Å.

Additional portions of the sample were analyzed for hydrogen by three methods: one portion by combustion of the hydride in a stream of oxygen, one portion by thermal decomposition and measurement of the hydrogen evolved, and several portions by reaction of the hydride with acid to give an amount of hydrogen which could be accurately measured. The formula was found to be YbH_{2.55} ± 0.06. The f.c.c. phase then would correspond ideally to the compound YbH₃, and thus unexpectedly be analogous to the trihydrides of the lighter rare-earths.

It was verified by an X-ray diffraction powder photograph that thermal decomposition of YbH_{2.55} in hydrogen at approximately one atmosphere yielded the orthorhombic dihydride. The formula of the dihydride was found to be YbH_{1.95} ± 0.05, by measurement of the hydrogen evolved from the

(2) W. L. Korst and J. C. Warf, *Acta Cryst.*, **9**, 452 (1956).

(3) T. R. P. Gibb, Jr., J. J. McSharry and R. W. Bragdon, *J. Am. Chem. Soc.*, **73**, 1751 (1951).

(4) Purchased from Research Chemicals, Burbank, California.

(5) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(6) G. Libowitz and T. R. P. Gibb, Jr., *ibid.*, **60**, 510 (1956).

YbH_{2.55}, as well as by analysis of the resulting dihydride. A metastable f.c.c. modification of ytterbium dihydride with *a* 5.26 Å. also was found when samples of YbH_{2.55} were thermally decomposed and quenched.

Measurement of the magnetic susceptibility of the YbH_{2.55} at room temperature by the Gouy method gave a molar susceptibility of 5040 × 10⁻⁶ c.g.s. unit. This compares quite reasonably with the value 7260 × 10⁻⁶ c.g.s. unit/mole⁷ which would be expected for a hypothetical YbH₃, containing only Yb⁺³ and H⁻ ions.

We also attempted to prepare a higher europium hydride by treating two small (30 mg.) pieces of the metal with hydrogen in the high-pressure apparatus in two separate experiments (33-41 atm. and 400-500°), but both attempts resulted only in the formation of the orthorhombic EuH_{1.8-1.9}. Perhaps EuH₃ was formed, but reverted to the dihydride when ordinary conditions were restored. It is also possible, since europium(II) is thermodynamically more stable than ytterbium(II) relative to the respective trivalent states, that no EuH₃ phase could be formed under the prevailing conditions. We succeeded, however, in preparing another sample of the higher ytterbium hydride from approximately 100 mg. of ytterbium metal. An X-ray diffraction powder photograph of the resulting hydride showed the presence of a large portion of the orthorhombic YbH₂ along with the f.c.c. phase. Analysis of a portion of this product gave the formula YbH_{2.2}.

We are pleased to acknowledge the financial support of the Office of Naval Research.

(7) G. Hughes and D. W. Pearce, *ibid.*, **55**, 3277 (1933).

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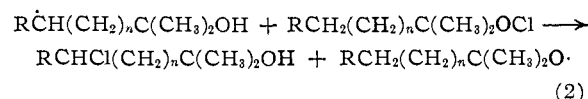
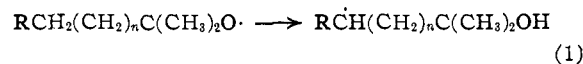
KENNETH HARDCASTLE

RECEIVED MARCH 20, 1961

INTRAMOLECULAR CHLORINATION WITH LONG CHAIN HYPOCHLORITES¹

Sir:

As part of our study of the radical reactions of alkyl hypochlorites^{2,3} we have been investigating the possibility of rearrangement of long-chain alkyl hypochlorites to chloroalcohols analogous to Hofmann-Löffler-Freytag reaction of N-chloroamines⁴ *via* a radical chain process involving sequences such as



(1) Work supported in part by a Grant from the National Science Foundation.

(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).

(3) C. Walling and W. Thaler, *ibid.*, in press.

(4) Conclusive proof of the radical chain nature of the Hofmann-Löffler-Freytag reaction and a review of older work has been given by E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).